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METAL VAPOR VISIBLE LASER KINETICS PROGRAM

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Avco Everett Research Laboratory,
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METAL VAPOR VISIBLE LASER KINETICS PROGRAM

SEMI ANNUAL TECHNICAL REPORT

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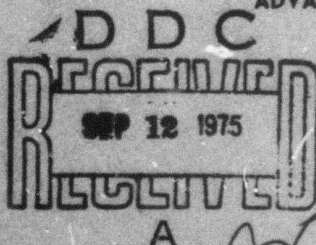
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13. ABSTRACT

Objective: The objective of this program is to investigate experimentally and theoretically the important kinetic rate constants pertinent to the development of a high power visible laser. This research consists of three tasks. Each of the tasks are summarized below.

TASK I Lower Level Kinetics (Experimental)

Objective: The purpose of this task is to identify metal atoms systems that allow selective collisional relaxation processes to efficiently quench lower levels of potential laser transitions. The present experimental study is directed to kinetic rate constant measurements for collisional deactivation of low lying optically metastable states of lead and copper.

Accomplishments: The flash photolysis apparatus developed under a prior ARPA contract was modified to provide temperature variability over the temperature range 300-600°K. Under the current program, this apparatus has been used to provide temperature dependent rate constant data for collisional deactivation of two low lying optically metastable states of atomic lead. The apparatus is now being adapted toward providing similar data for copper at 600°K.

TASK II Upper Level Kinetics (Experimental)

Objective: The purpose of this task is to determine the efficiency of various quenchant in deactivating the upper laser level of lead. To be useful, a quenchant must rapidly relax the lower laser level and slowly relax the upper laser level, i.e. be selective.

Accomplishments: A new experimental fluorescence apparatus, which utilizes d.c. phase sensitive detection techniques is currently being assembled and tested. Preliminary experiments on Hg fluorescence have been performed for system checkout and evaluation purposes.

TASK III Excitation Processes (Theoretical)

Objective: The objective of this effort is to calculate electron impact excitation and quenching cross sections for the upper and lower laser levels of the metal atoms of interest.

Accomplishments: This theoretical effort has recently begun with initial steps taken to formulate the basic approach and begin preliminary calculations.

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1. Electronic State Collisional Relaxation Kinetics
2. Metastable Atom Quenching
3. Temperature Dependence of Metastable Atom Relaxation
4. Electronically Excited Lead Atoms
5. Electronically Excited Copper Atoms
6. Resonance Fluorescence
7. Resonance Absorption
8. Electron Excitation Cross Sections
9. Electron Mixing Cross Section

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FOREWORD

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TASK I

LOWER LEVEL KINETICS

1.1 INTRODUCTION

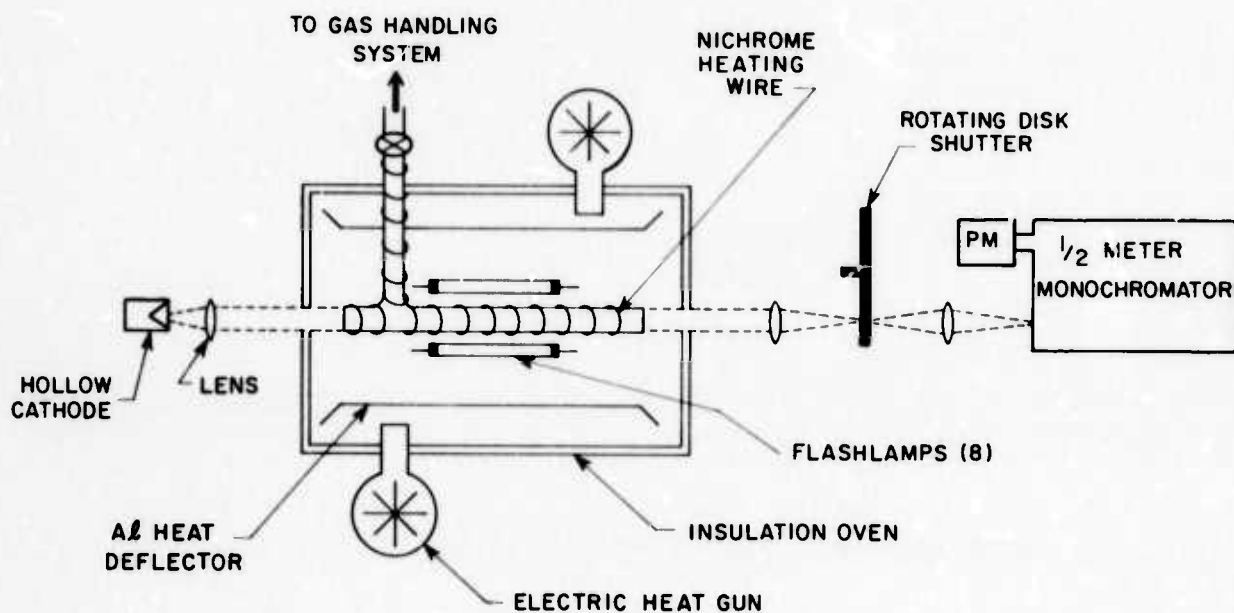
The requirements of a high power, efficient, visible laser place the following general constraints on likely laser candidates: (1) the visible wavelength requirement defines the transition as an electronic transition; (2) the upper laser level should be rapidly and selectively pumped either by direct electron excitation or through heavy particle resonant energy transfer processes; (3) for good quantum efficiency, the lower level should not be too high in energy or the laser transition would represent too small a fraction of the required excitation energy; and (4) the lower laser level must be rapidly and selectively relaxed by volumetric processes. These requirements can in principal be met with electronic transitions occurring in various metal atoms from low lying resonance levels to lower lying optically metastable states. The rates and mechanisms whereby these low lying metastable electronic energy levels are deactivated in collisions with simple atoms and molecules is the subject of this Task. It consists of two subtasks: (1) a measurement of the temperature dependence from 300-600°K of collisional relaxation rate constants for the $6p^2$ (3P_2) and (3P_1) states of atomic lead; and (2) similar measurements for the $3d^9 4s^2$ ($^2D_{5/2}$) and ($^2D_{3/2}$) states of atomic copper near 600°K.

1.2 TEMPERATURE DEPENDENT LEAD RELAXATION KINETICS

The rates and mechanisms whereby optically metastable electronic states of atoms are deactivated in collisions with simple atoms and molecules have been investigated for a variety of atomic species.⁽¹⁾ The observed

collisional deactivation rate constants have been interpreted in terms of curve crossings, curve mergings, chemical reactions, and $E \rightarrow V$ (electronic to vibrational) energy transfer processes. Such mechanisms are suggested as possible explanations for the observed rate data but are explanations based only on plausibility arguments. For example, $E \rightarrow V$ energy transfer has been offered as the principal de-excitation mechanism for a variety of systems but direct proof has only recently been obtained for the relaxation of the $^2P_{1/2}$ state of Br upon collisions with HBr and HCl.⁽²⁾ Aside from the difficult problem of direct observation of the energy branching into the product channels, the usual approach used to unravel the observed de-excitation phenomena is to consider which paths are more probable within a theoretical framework and then test model predictions with further experimentation. The simplest test of any model is to compare predicted temperature dependence to observed experimental data. Surprisingly, temperature dependent rate data for collisional de-excitation of optically metastable electronic states of atoms is limited to Iodine,⁽³⁾ Arsenic⁽⁴⁾ and Thallium.^(5,6) We report here measurements for the collisional quenching of the $6p^2 (^3P_2)$ and $6p^2 (^3P_1)$ states of atomic lead over the temperature range 300 to 560°K by collisions with Ar, Xe, N_2 , D_2 , H_2 and by Hg at 373°K.

The apparatus, whose basic design is shown in Fig. 1, was similar to our room temperature facility⁽⁷⁾ except for the following modifications: (1) The addition of Nichrome heating wire wound in a spiral over the entire surface of the reaction cell at approximately 8 mm intervals and (2) the enclosure of the reaction cell and flashlamps in an insulated box attached to which are two electric heat guns. In this way, reaction cell temperatures



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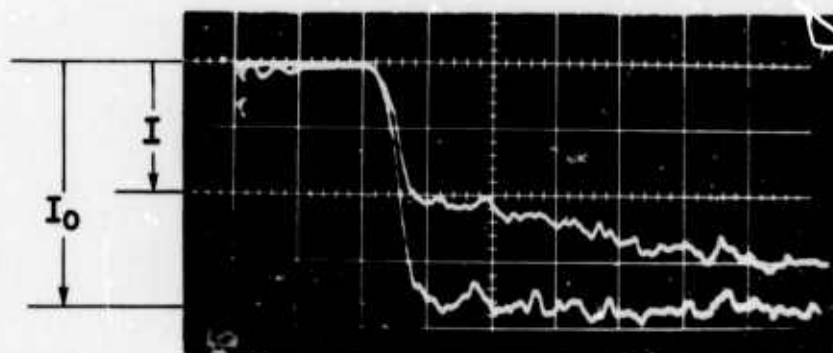
Fig. 1 Schematic Diagram of Lower Level Kinetics Apparatus

in excess of 600°K were easily obtained as determined by thermocouples placed at various locations on the glassware surface.

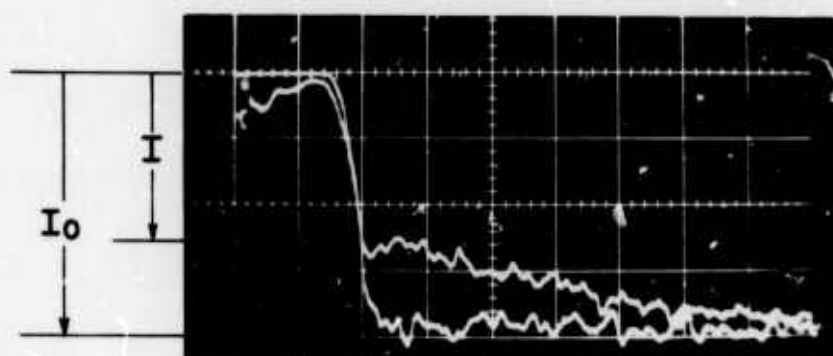
The experimental procedure remains essentially unchanged from the techniques used at room temperature⁽⁸⁾ and simply consists of introducing premixed gases into the heated reaction chamber for subsequent photolysis. These mixtures consist of 50 to 100 torr of Ar containing 1 ppm of (CH₃)₄ Pb and varying amounts of the quenchant under investigation. The ³P₂ and ³P₁ states of Pb are produced by the multi-photon photodecomposition of the tetramethyl lead. The production and subsequent decay of these metastable states are monitored utilizing time resolved line absorption techniques at 4058 and 3683 Å respectively. Typical data showing the relaxation of the ³P₂ state of Pb in 50 torr of Ar, 0.05μ of TML, and 62μ of H₂ are shown in Fig. 2. Such data are interpreted utilizing the modified Beer-Lambert Law and the observed first order decay for the data of Fig. 2 is shown in Fig. 3. Additional data taken at 298, 500 and 560°K for varying amounts of added Hydrogen are shown in Figs. 4, 5, and 6. The slopes of these plots were obtained from least square computer techniques and then converted to bimolecular (second order) rate constants and subsequently fitted to Arrhenius functions, i. e. $k = A \exp (-E_a/RT)$, by plotting log k vs. 1/T. An Arrhenius plot using the data of Figs. 4, 5, and 6 is shown in Fig. 7. Similar procedures were performed for the other quenchants. The resulting rate constants and Arrhenius parameters are summarized in Tables I and II, respectively. In general, little temperature variation of these rate constants was observed.

1.3 COPPER RELAXATION KINETICS

The results of this sub-task will be included in the final report.



50 TORR AR
0.05 μ Pb (CH₃)₄



50 TORR AR
0.05 μ Pb (CH₃)₄
62 μ H₂

50 μ SEC

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→ TIME

Fig. 2 Decay of 3P_2 Pb Atoms Monitored at 4058 Å

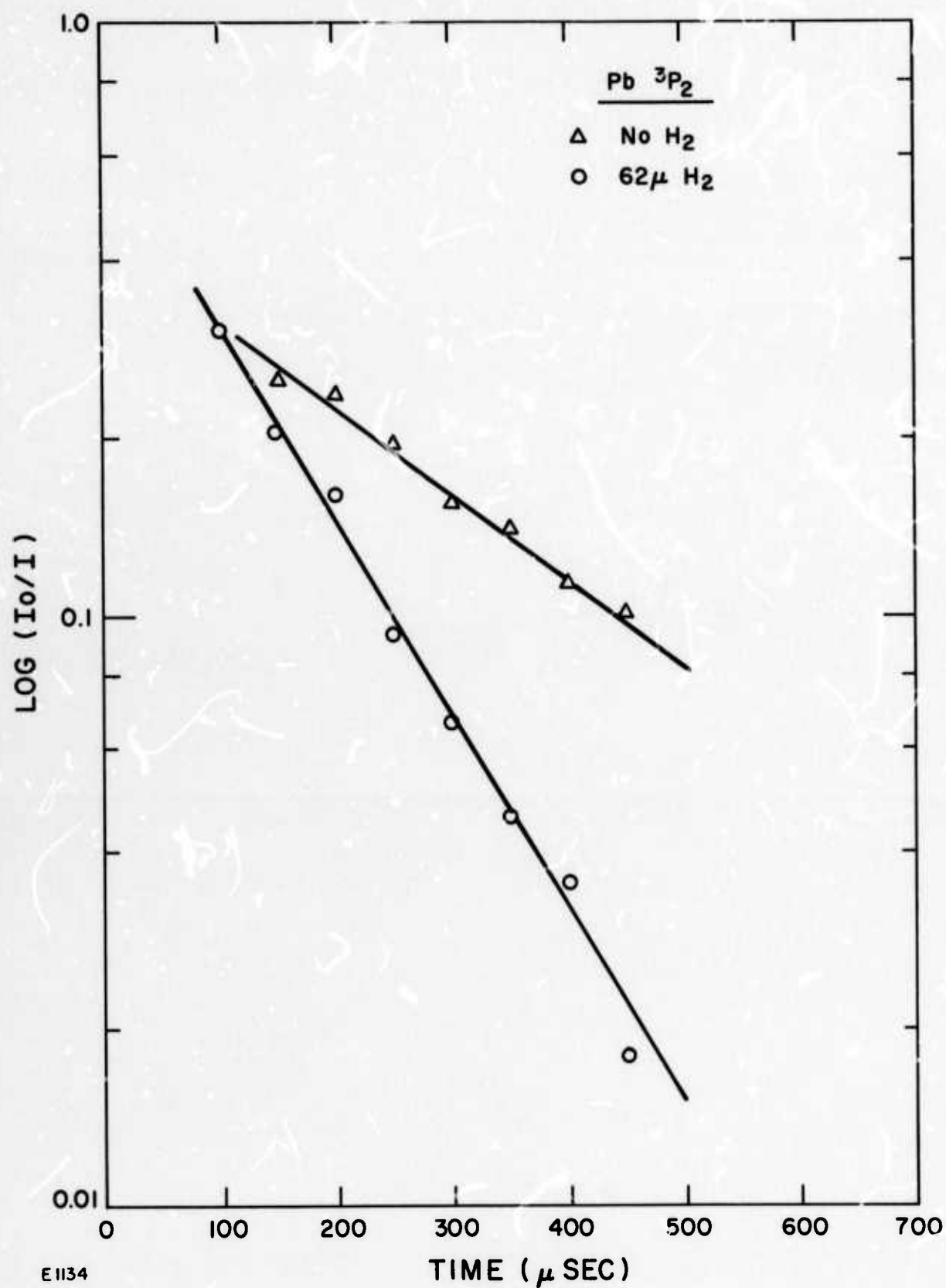
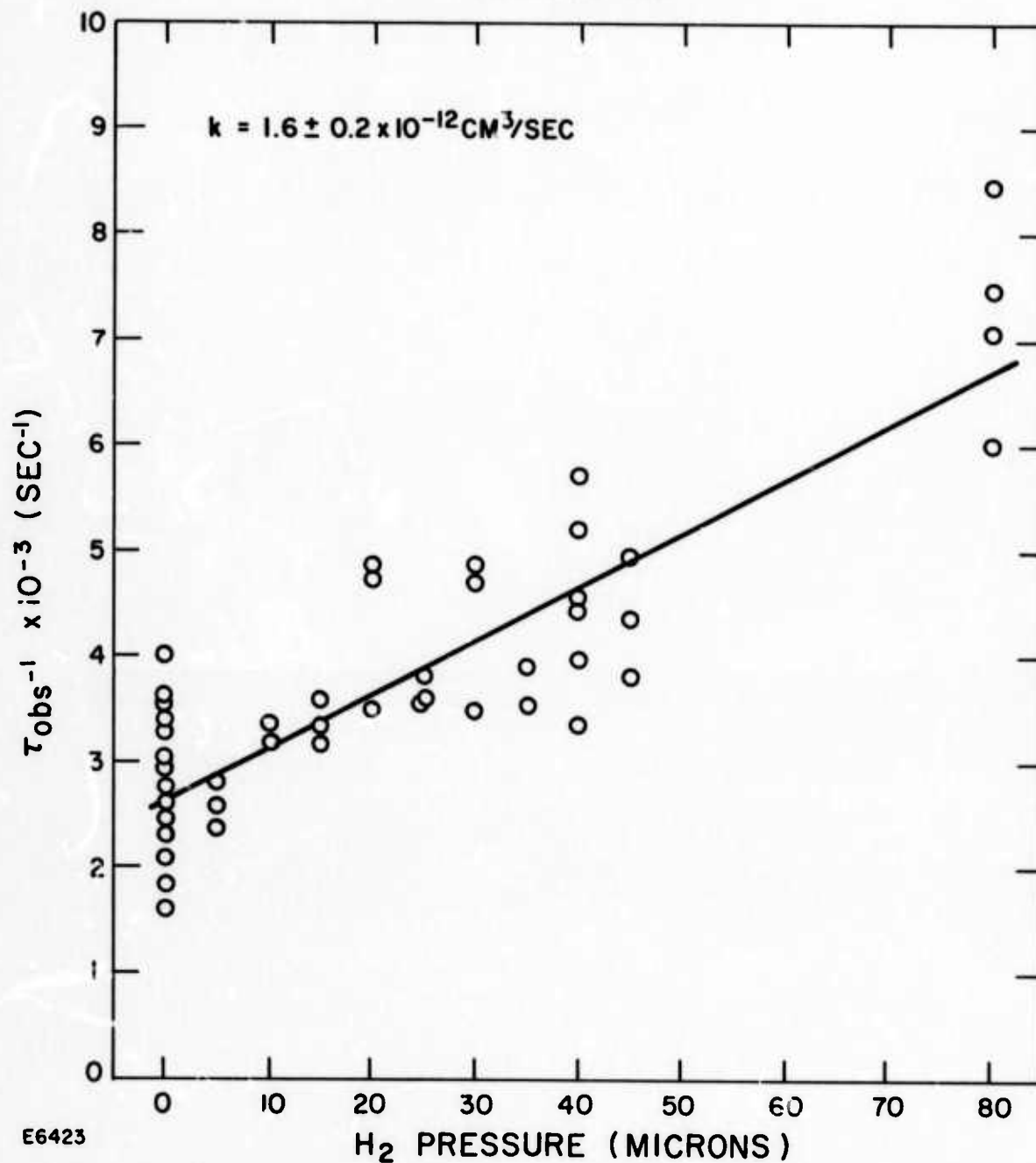
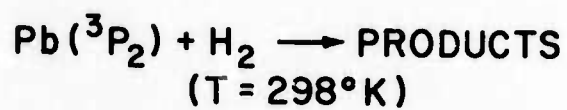
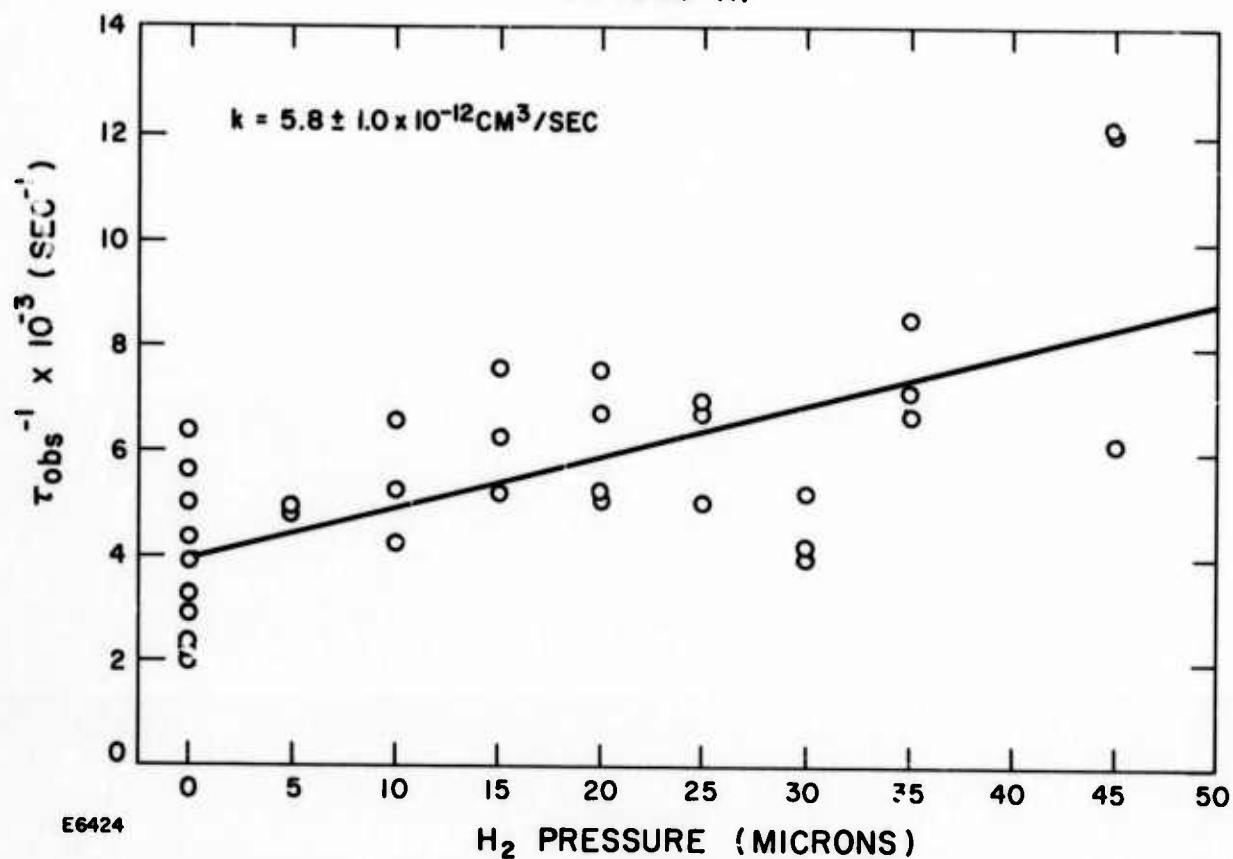
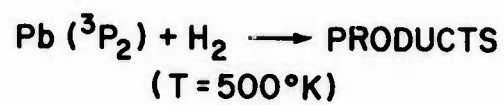


Fig. 3 Log (I₀/I) vs Time Plot for Data of Fig. 2



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Fig. 4 Plot of Pseudo-First-Order Rate Constant τ^{-1} vs PH_2 at 298°K



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Fig. 5 Plot of Pseudo-First-Order Rate Constant τ^{-1} vs PH_2 at 500°K

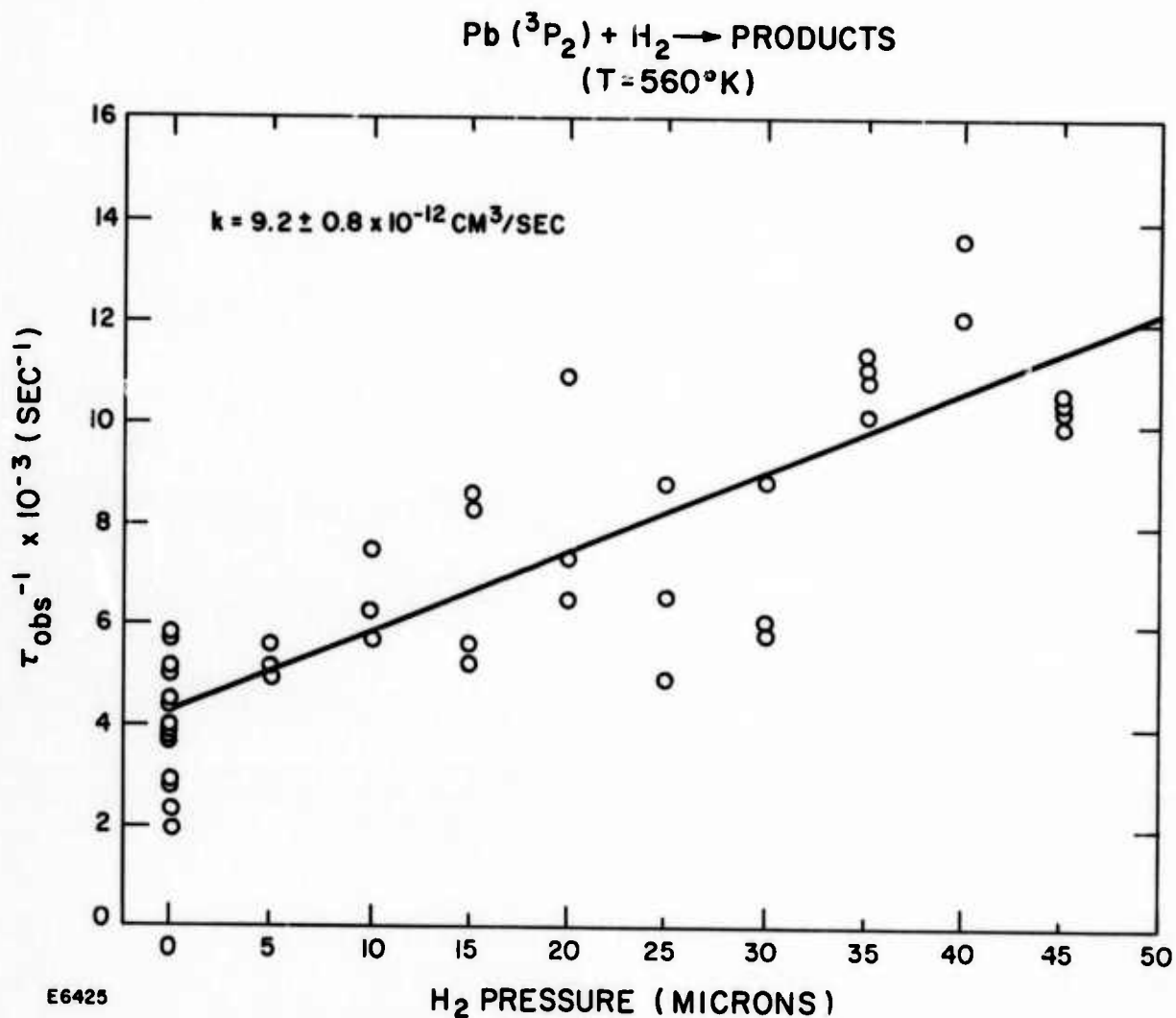


Fig. 6 Plot of Pseudo-First-Order Rate Constant τ^{-1} vs PH_2 at 560°K

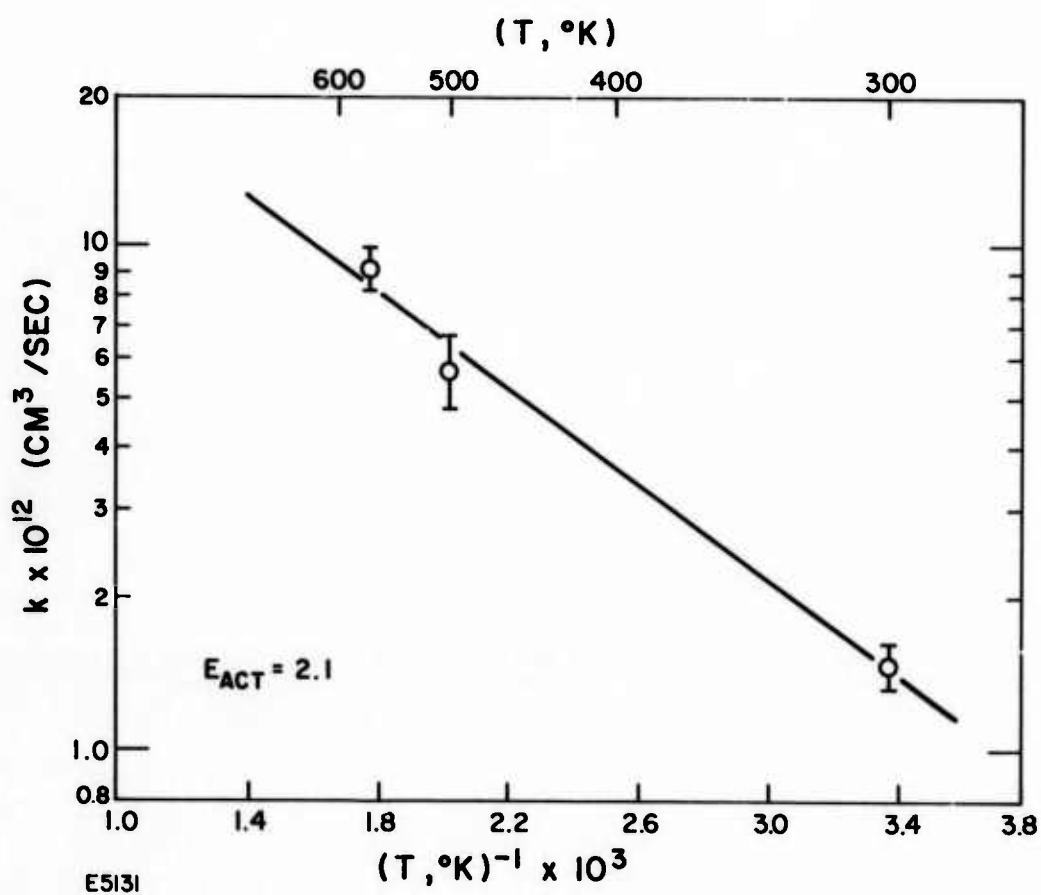


Fig. 7 Arrhenius Plot for the Reaction $\text{Pb}(^3\text{P}_2) + \text{H}_2$ from Data of Figs. 4, 5 and 6

TABLE I
SUMMARY OF KINETIC RATE CONSTANTS

Reaction	298°K	k (cm ³ /sec)	500°K	555°K
$^3P_1 + Ar$	$< 1.7 \pm 0.4 \times 10^{-16}$	$< 2.1 \pm 0.3 \times 10^{-16}$	$< 2.6 \pm 0.5 \times 10^{-16}$	
+ Xe	$< 1 \times 10^{-16}$			
+ N ₂	$< 8.5 \pm 0.6 \times 10^{-16}$	$< 9.4 \pm 0.8 \times 10^{-16}$	$< 7.9 \pm 1.0 \times 10^{-16}$	
+ D ₂	$< 2.6 \pm 1.5 \times 10^{-16}$	$< 8.6 \pm 1.5 \times 10^{-16}$	$< 5.5 \pm 1.4 \times 10^{-16}$	
+ H ₂	$1.5 \pm 0.3 \times 10^{-15}$	$8.7 \pm 0.5 \times 10^{-15}$	$1.3 \pm 0.1 \times 10^{-14}$	
$^3P_2 + Ar$	$< 2.4 \pm 0.9 \times 10^{-15}$	$< 4.2 \pm 1.5 \times 10^{-15}$	$< 4.4 \pm 1.1 \times 10^{-15}$	
+ Xe	$< 3 \times 10^{-15}$			
+ N ₂	$3.5 \pm 1.3 \times 10^{-13}$	$10 \pm 2 \times 10^{-13}$	$9.0 \pm 2.1 \times 10^{-13}$	
+ D ₂	$7.7 \pm 0.5 \times 10^{-12}$	$14 \pm 2 \times 10^{-12}$	$14 \pm 1.4 \times 10^{-12}$	
+ H ₂	$1.6 \pm 0.2 \times 10^{-12}$	$5.8 \pm 1.0 \times 10^{-12}$	$9.2 \pm 0.8 \times 10^{-12}$	
$^3P_1 + Hg$	$k \leq 1.3 \pm 0.4 \times 10^{-14} \text{ cm}^3/\text{sec} (373^\circ K)$			
$^3P_2 + Hg$	$k \leq 1.6 \pm 0.4 \times 10^{-14} \text{ cm}^3/\text{sec} (373^\circ K)$			

TABLE II
KINETIC RATE CONSTANTS
(Arrhenius Parameters)

Reaction	A (cm ³ /sec)	E _A (kcal)
$^3\text{P}_1 + \text{H}_2 \rightarrow$	1.3×10^{-13}	2.7
$^3\text{P}_2 + \text{H}_2 \rightarrow$	5.7×10^{-11}	2.1
$^3\text{P}_2 + \text{D}_2 \rightarrow$	2.9×10^{-11}	0.8
$^3\text{P}_2 + \text{N}_2 \rightarrow$	3.4×10^{-12}	1.3

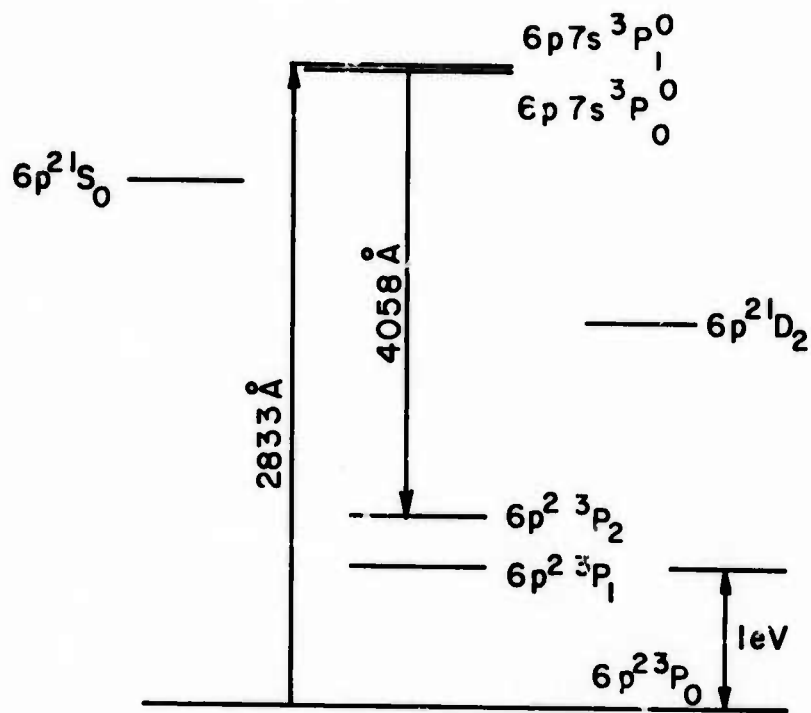
TASK II

UPPER LEVEL KINETICS

It is the goal of this experiment to measure the cross section for collisional quenching of the upper $6p7s\ ^3P^o_1$ state of Pb by various buffer gases. An energy level diagram of the relevant states of Pb for laser application is given in Fig. 8. The ultimate aim of this program is to identify buffer gases which have quenching cross sections for the upper laser state of Pb that are smaller than those found for the lower metastable levels of Pb. This will allow the use of selective quenching for a collision dominated $4058\ \text{\AA}$ Pb laser.

The experimental apparatus presently being set up is shown schematically in Fig. 9. Resonance radiation ($2833\ \text{\AA}$) is taken from a hollow cathode source and is chopped and focused into a suprasil quartz cell which contains Pb at $\sim 570^\circ\text{C}$ ($p(\text{Pb}) \sim 10^{-4}$ Torr). A fluorescence $4058\ \text{\AA}$ signal is observed perpendicular to the incoming signal. This signal is fed into a lock-in amplifier for improved signal to noise. Once the signal level for pure Pb has been established, various buffer gases, e. g., CO_2 , H_2 , D_2 , He etc. will be added and the resulting decrease in fluorescence due to collisional quenching will be observed. This will allow the graphing of a Stern Volmer⁽¹⁰⁾ type plot for each buffer gas. One is able to deduce the collisional quenching cross section from such a plot.

Preliminary measurements have been made of the resonance fluorescence from Hg in the setup as shown in Fig. 9. Hg was used as a test case since it allows one to avoid the problems associated with having a hot (570°C) cell. Fluorescence signals with adequate signal to noise have been observed.



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Fig. 8 Partial Energy Level Diagram for Lead Electronic States

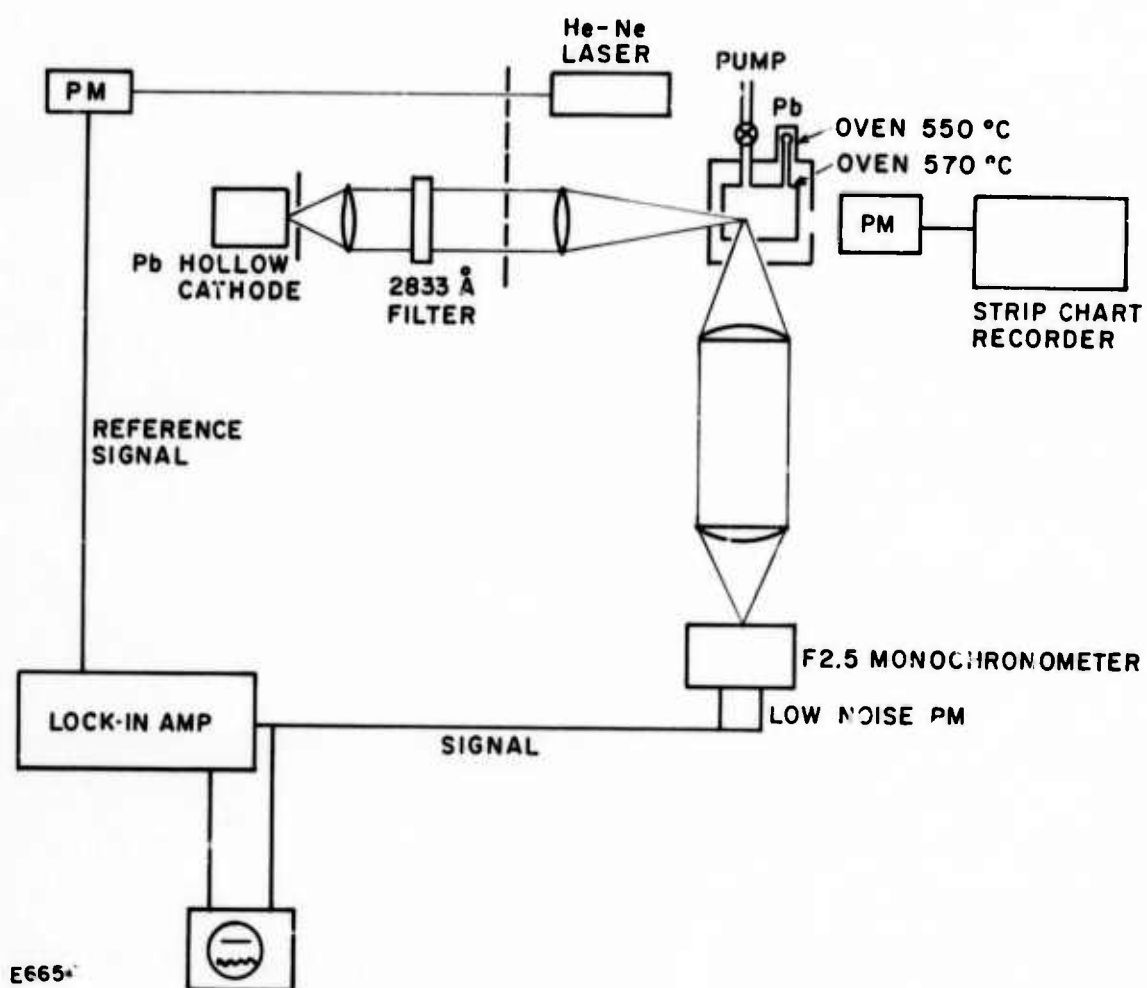


Fig. 9 Schematic Diagram of Upper Level Kinetics Apparatus

TASK III

EXCITATION PROCESSES

The goal of the theoretical task is to calculate excitation and quenching cross sections, due to electron impact, for the upper and lower laser levels of the atoms of interest. In particular, we are concentrating upon the relevant rates for the copper laser.

To obtain the required cross sections, two somewhat distinct problems must be addressed: (1) the internal structure of the target atom, and (2) the dynamical problem associated with the colliding electron. The former problem presents considerable difficulties in the case of the copper atom. Copper, in its ground state, has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s$; however, the 3d electrons are fairly loosely bound so that configuration interaction effects due to "core-excited" states become very important (e. g., see Ref. 11). As an example, the $3d^9 4s 4p$ terms mix with higher-lying $3d^{10} np$ levels, and this situation makes an a priori calculation very difficult. However, the so-called optical oscillator strengths (f-values), between dipole-connected levels, take these configuration interaction effects into account. Since these f-values are known accurately from experiment for the states of interest, we will use them to calculate the electron impact cross sections between optically-connected levels. Having adopted this dipole approximation, several methods are available for the dynamical aspect of the problem, those due to Seaton⁽¹²⁾ being particularly useful. In addition, Seaton's impact parameter theory, which takes both reciprocity and unitarity into account, has been extended by Stauffer and McDowell⁽¹³⁾ to transitions due to

arbitrary multipoles of the interaction potential. This extended theory can then be applied to excitation of the lower laser level, $3d^9 4s^2$, which is expected to be strongly quadrupole-connected to the ground state due to the large overlap between the 3d and 4s wavefunctions. Since this transition is optically forbidden, we have no experimental f-value to use, and the quadrupole moment will have to be calculated from first principles. For this purpose, it is planned to use the Hartree-Fock-Slater computer program of Herman and Skillman⁽¹⁴⁾ to generate the required wavefunctions. At present, we have just begun to implement the computational methods described above.

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